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Final Technical Report

Contract AFOSR-73-2460

By

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Gas-liquid critical constants have been measured for fluorinated ethanes and used to test empirical corresponding states relations for the determination of molecular force constants. These empirical relations appear to be applicable to essentially all substances for which critical data are available. A radio-tracer technique has been developed for the investigation of unimolecular collisional energy transfer for $^{14}\text{CH}_3\text{CF}_3$ activated by $^{14}\text{CH}_3$ plus CF_3 recombination. This method has yielded a significant improvement in sensitivity with respect to existing techniques. It appears to be widely applicable for		

20. continued

high accuracy studies of unimolecular reactions.

AFOSR Final Technical Report

Under contract AFOSR-73-2460 the following projects were investigated at U.C. Davis during the period October 15, 1972 through December 31, 1975:

1. Molecular Force Constants From Gas-Liquid Critical Constants.

Dr. Frank E. Little has just completed his Ph.D. Dissertation involving experimental measurements of gas-liquid critical constants for C_2H_6 and all the fluoroethane isomers. The semi-empirical molecular size analysis described in our prior AFOSR proposals appears to be applicable to virtually all substances, possibly excepting the low-temperature quantum fluids. However, based upon the limited amount of available data, anomalous behavior was indicated for the fluoroethanes. We thus initiated an experimental investigation of these substances in the hope of developing an independent validity test for the revised corresponding states analysis.

The experimental results substantiated the unusual excluded volume behavior of fluorinated ethanes and further showed a marked dependence of the critical temperature upon isomer structure, which was unusually large for organic substances. A straightforward explanation of this T_c behavior followed from the analysis of dipole-dipole and dipole-induced-dipole interactions for these substances.

As indicated above, we had originally hoped to achieve some degree of corroboration for the corresponding states analysis, which seemed both too simple and too successful to be readily believable. However, the fluoroethane study actually compounded this credibility problem by demonstrating that not only the length parameter but also the well-depth molecular force constant could be reliably predicted from simple corresponding states assumptions.

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After five years of thinking and experimentation, we have not been able to devise any suitably accurate independent testing procedure short of comprehensive molecular beam elastic cross section measurements. This latter approach would be very costly, both in money and time. It thus appears that we should publish the entire study all at once, using the universality of the method to argue for its validity.

2. Chemical Activation Unimolecular Kinetics and Collisional Energy Transfer.

Our second major success followed from the continuation of the $^{14}\text{CH}_3\text{CF}_3$ unimolecular kinetics research, which was initiated as the AFOSR-68-1493 supported Ph.D. Dissertation of Dr. G. W. Mutch.

At the beginning of AFOSR-73-2460 the first rather primitive kinetics experiments and related theoretical calculations had just been completed. These results have since been published. During the second year of AFOSR-73-2460, Dr. Richard Pettijohn took up the continuation of this project. Experiments at very low pressures revealed that the radiotracer technique provided heretofore unattainable sensitivity for unimolecular collisional energy transfer experiments.

Unimolecular kinetics is an established discipline with an immense literature and many eminent authorities, both in the U.S. and abroad. The theory is sufficiently challenging that few researchers undertake this type of research apart from individuals receiving graduate or post-graduate training in it. We were thus surprised to be in the apparent position of having developed a technique surpassing the capability of the best previous technology. Though AFOSR personnel may find this attitude difficult to appreciate, we were uncomfortable about this situation both because of the sheer magnitude of the existing unimolecular energy transfer literature and of the very outstanding abilities of several U.S. specialists,

notably Prof. B. S. Rabinovitch (University of Washington) and several of his former associates.

The following quotation has been taken from a letter (12/1/75) from Prof. Rabinovitch with whom we corresponded about our early results:

"Incidentally, although in our own work we have never really gotten down below S/D values of 0.01, one of the unsuccessful mainstreams of our efforts in the period 1965 to 1975 was the attempt to find a straight-forward chemical activation system which would permit us to go much farther in the "turn up" region and to define the whole turn up region with much greater accuracy than we had hereto succeeded in doing. Most of those efforts appeared simply as spin-off studies in radical isomerization, disproportionation, and in methylene radical chemistry. We did not succeed in our purpose. Such data would be very valuable for the precise distribution function. There has not really been any significant progress by anyone so far past our original conclusion that weak collisions seem to be exponential or Poisson-like in nature, while strong collisions are step ladder, or, more realistically, gaussian in nature. The paper by Lin and myself in JPC, August or September (1970) gives a theory as to why this is reasonable, but good data of high accuracy are still wanting." In order to put the current $^{14}\text{CH}_3\text{CF}_3$ experiments in perspective vis-a-vis Prof. Rabinovitch's comments, we have succeeded in attaining S/D values of 5×10^{-4} . With improvements, we believe that considerably smaller limiting S/D ratios will ultimately be possible. In view of the possible significance of this work, we have been very anxious to be certain of both the data and their theoretical interpretation. Both of these goals have now been accomplished, and a major paper is now in the final stages of preparation.

3. Stopping Power Project.

Now we turn to our failures. Listed at the end of the final report for contract AFOSR-68-1493 were several "in preparation" technical publications based upon the Ph.D. Dissertation of Dr. Larry L. Lucas, which was completed just prior to the termination of AFOSR-68-1493. The preparation of these papers should have been an important objective during the early part of AFOSR-73-2460. It has, however, been Prof. Root's longstanding policy that Ph.D. students must assist with the literature documentation of their research results. Dr. Lucas' work is both novel and of good quality, but he has adamantly refused to cooperate in the matter of its publication. This has been a source of considerable personal embarrassment to Prof. Root, which in part accounts for the delay of this final report.

4. Variable Wavelength Photodissociation Program.

Here, too, the record is disappointing. Two of the manuscripts listed in the previous final technical report were actually written. The first paper dealing with reactions of energetic CH₂T radicals with H₂ received excellent reviews and was provisionally accepted at J. Amer. Chem. Soc. pending minor revisions. As a result of the combination of Prof. Root's busy schedule and his lack of experience in dealing with postdocs, Dr. Tsao was allowed to carry out these experiments without extensive participation by Prof. Root with the laboratory work itself. At the time this seemed quite reasonable on the strength of Dr. Tsao's technical qualifications.

Prof. Root first began to have doubts concerning Dr. Tsao's data about halfway through the Brookhaven sabbatical. Based upon closer analysis of these results, the J. Am. Chem. Soc. manuscript was withdrawn

pending the acquisition of further data. The problem, which was not unsolvable, was one of simple signal-to-noise. Its resolution would have necessitated basic changes in Dr. Tsao's method of radioassay. During the brief remainder of his tenure at Davis, he was unable to accomplish this or to satisfy Prof. Root that his data were meaningful. Prof. Root was extremely reluctant to drop this work because of its exciting potential, and he still considers the method to be basically sound. However, he was also reluctant to seek further AFOSR support for it in the face of this lack of demonstrable success.

5. Status of Publications.

As indicated above, the Mutch thesis has been published. At least one long paper could follow from the Little thesis, and several from the Lucas thesis (Prof. Root has just approached him again about this). There is also the low-pressure unimolecular collisional energy transfer study, and the prior work on molecular force constants.

Our understanding of current Amer. Chem. Soc. journal editorial policy is that page charge waivers cannot be granted for contract-supported research. The Amer. Inst. of Physics journals have no such restriction, but manuscripts are intentionally delayed for a year or more if page charges cannot be honored. Dr. Root has a more-or-less continuous backlog of technical writing, even though he has recently been publishing at the rate of several long papers per year. It would greatly facilitate the appearance of this AFOSR supported research if some provision could be made for AFOSR to cover these page charges. No other funds are available to Dr. Root for this purpose.

6. Scientific Personnel.

Dr. John W. Root, principal investigator.

Dr. Chi-Wing Tsao, postdoctoral research associate.

Dr. Richard R. Pettijohn, postdoctoral research associate.

Dr. Frank E. Little, graduate student (Ph.D. 1976).

Dr. George W. Mutch, graduate student (Ph.D. 1973).

Dr. James F. Harrison, postdoctoral research associate (computer software specialist hired to assist with program development).

Mr. Ira V. Ellenbogen, hourly computer programmer.

Ms. Gloria J. Young, undergraduate laboratory helper (hired on an hourly basis to assist Dr. Mutch with experiments and numerical data analysis).

Ms. Jennifer Fujimoto, undergraduate technician (hired on an hourly basis to prepare line drawings of results).

7. Bibliography.

1. Chemically Activated $^{14}\text{CH}_3\text{CF}_3$ from Cross Combination of $^{14}\text{CH}_3$ with CF_3 . An Introductory Experimental Study. R. R. Pettijohn, G. W. Mutch, and J. W. Root, *J. Phys. Chem.* 79, 2077 (1975).

2. Details of Radiogaschromatography Apparatus. R. R. Pettijohn, G. W. Mutch, and J. W. Root, Microfilm supplement to Ref. 1.

3. Chemically Activated $^{14}\text{CH}_3\text{CF}_3$ from Cross Combination of $^{14}\text{CH}_3$ with CF_3 . II. Collisional Energy Transfer to Fluorinated Ethanes. R. R. Pettijohn, G. W. Mutch, and J. W. Root, *J. Phys. Chem.* 79, 1747 (1975).

4. Details Concerning 6-Channel Solid-State Buffered Memory Scaler. R. R. Pettijohn, L. L. Lucas, and J. W. Root, AFOSR Technical Report,

U.C. Davis, 1975. This report has been completed, but has not been reproduced for distribution owing to lack of funds.

5. Future Technical Publications as detailed in Section 5.

8. Dissertations.

1. Studies of Corresponding States Potential Force Constant Scaling Relations and the Critical Constants for the Fluoroethanes. Frank E. Little, Ph.D., 1976.